Registry No. $(C_4H_4N_2)Os_3(CO)_{10}$, 63833-62-5; $Os_3(CO)_{12}$, 15696-40-9; ^{13}C, 14762-74-4.

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Syntheses and Optical and Magnetic Properties of Tetrakis(di-*n*-propylamido)uranium(IV), Tetrakis(di-*n*-butylamido)uranium(IV), Tetrakis(di-*n*-propylamido)thorium(IV), and Tetrakis(di-*n*-butylamido)thorium(IV), Volatile Liquid Amides

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The thorium and uranium alkylamides $M[N(CH_2CH_2CH_3)_2]_4$ and $M[N(CH_2CH_2CH_2CH_3)_2]_4$ (M = Th and U) have been prepared and isolated. These extremely air-sensitive compounds are liquids at room temperature and distillable under high vacuum at temperatures less than 100 °C. The proton magnetic resonance spectra, the optical spectra, and the temperature-dependent magnetic susceptibilities (T = 4.2–100 K) of the two uranium compounds are reported. The spectroscopic and magnetic properties of the uranium compounds are very similar to those of $U(N(C_2H_5)_2)_4$.

Introduction

Transition metal amides have been utilized as reactive intermediates in the synthesis of transition metal alkoxides, thiols, and organometallic derivatives.[1] Recently, we have reported many new uranium amides, which are not only useful as extremely reactive intermediates[2,3] but exhibit novel physical properties.[4-7] In the solid state, these new uranium compounds have exhibited monomeric,[6] dimeric,[4] trimeric,[5] and tetrametric[7] molecular units, with the U atoms being bridged by N atoms. The coordination about the U atom is four, five, or six in the crystals, while in solution the coordination about the U atom depends on the complexing ability of the solvent. In order to extend this work, we now report the preparation and isolation of the actinide amides $U[N(CH_2CH_2CH_3)_2]_4$ and $U[N(CH_2CH_2CH_2CH_3)_2]_4$ and their thorium analogues. These compounds are liquids at room temperature, and their physical and solution properties are markedly similar to those of $U(NEt_2)_4$[4,8] and $Th(NEt_2)_4$,[9] respectively.

Experimental Section

Solvents. All solvents were dried and deoxygenated by refluxing with sodium and benzophenone under purified argon.

Reagents and Synthesis. All reactions and manipulations were done either under vacuum or in a purified argon atmosphere. The amines were purchased from the Aldrich Chemical Co. *N*-Butyllithium was purchased from Alfa-Ventron Corp. and used as delivered.

$LiNR_2$. These compounds were prepared by the slow addition of the amine mixed with pentane (dried with KOH, then Drierite) to *n*-butyllithium in hexane at ice bath temperatures. The resulting precipitate was filtered and vacuum dried.

UCl_4 and $ThCl_4$. These compounds were purchased from ROC/RIC and used as delivered.

$U(N(CH_2CH_2CH_3)_2)_4$. UCl_4 (10 g, 0.0264 mol) and 11.2 g (0.105 mol) of $LiN(CH_2CH_2CH_3)_2$ were placed in a 250-mL Schlenk flask. Approximately 100 mL of diethyl ether was transferred into the flask under vacuum at liquid N_2 temperature. The heterogeneous mixture was warmed to room temperature and continuously stirred during the reaction. The reaction times varied from 24 h to 7 days. The formation of a characteristic green solution and a LiCl precipitate indicated the completion of the reaction. The solution was then filtered and the filtrate reduced to a high-viscosity liquid by vacuum evaporation. This residue was placed in a distillation apparatus and distilled between 40 and 50 °C at 10^{-4} mmHg, yielding a green liquid product. The yields for this compound and the others reported in this paper were about 30–40%. Anal.[10] Calcd for $U(N(CH_2CH_2CH_3)_2)_4$: U, 37.3; C, 45.1; N, 8.77; H, 8.77. Found: U, 37.58; C, 44.69; N, 8.63; H, 8.54.

$U(N(CH_2CH_2CH_2CH_3)_2)_4$. This compound was synthesized on the same scale as above but with the following minor changes. Reaction time was extended to 8 weeks. The characteristic green solution was not observed for at least 4 weeks. The sublimation temperature range was 90–100 °C. Temperatures above 110 °C caused noticeable decomposition, distilling over some volatile decomposition products. Anal. Calcd for $U(N(CH_2CH_2CH_2CH_3)_2)_4$: U, 31.73; C, 51.20; N, 7.47; H, 9.60. Found: U, 31.85; C, 50.95; N, 7.23; H, 9.51.

$Th(N(CH_2CH_2CH_3)_2)_4$. This compound was synthesized by the same method as above but with the following changes. Reaction time was at least 7 days. The reaction was complete when a slight yellow tinge to the diethyl ether solution appeared since the $ThCl_4$ and LiCl suspensions are virtually indistinguishable under these conditions. The sublimation temperature range was 60–70 °C at 10^{-4} mmHg, yielding a clear light yellow liquid. This compound appeared to be photosensitive for the product slowly darkened after distillation. Anal. Calcd for $Th(N(CH_2CH_2CH_3)_2)_4$: Th, 36.70; C, 45.57; N, 8.86; H, 8.86. Found: Th, 37.03; C, 45.16; N, 8.86; H, 8.86.

$Th(N(CH_2CH_2CH_2CH_3)_2)_4$. This compound was synthesized by the same method as above except with the following changes. Reaction time was 6 weeks. Sublimation temperature was 90–100 °C at 10^{-4} mmHg, and temperatures above 110 °C caused noticeable decomposition. The distillation produced a clear light yellow liquid, also sensitive to heat and light. Anal. Calcd for $Th(N(CH_2CH_2CH_2CH_3)_2)_4$: Th, 31.18; C, 51.60; N, 7.53; H, 9.68. Found: Th, 30.86; C, 51.32; N, 7.38; H, 9.51.

Physical Measurements. Proton magnetic measurements were obtained on a Varian T-60 spectrometer, a Varian NV-14 spec-

Table I. Physical Properties of Some Uranium Amides

Compd	Phase[a]	Distillation temp,[b] °C
$U(N(CH_2CH_3)_2)_4$[4,8]	Solid	40–50
$U(N(CH_2CH_2CH_3)_2)_4$	Liquid	40–50
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Liquid	90–100
$Th(N(CH_2CH_3)_2)_4$[9]	Solid	40–50
$Th(N(CH_2CH_2CH_3)_2)_4$	Liquid	50–60
$Th(N(CH_2CH_2CH_2CH_3)_2)_4$	Liquid	90–100
$U(N(C_6H_5)_2)_4$[6]	Solid	Dec[c]
$U_3(CH_3NCH_2CH_2NCH_3)_6$[5]	Solid	Dec

[a] At room temperature. [b] At less than 10^{-4} mmHg pressure. [c] Decomposition without sublimation.

trometer, or a Varian 220-MHz spectrometer with Nicolet Fourier transform modifications. The latter two spectrometers were equipped with variable-temperature probes. The NV-14 spectrometer was equipped with a Minimite Model 238 temperature control unit equipped with a minimite thermocouple having an accuracy of ~1.0 °C. The Varian 220-MHz spectrometer was calibrated by a methanol standard. Samples were prepared by dissolving the purified amides in THF-d_8 or toluene to give solutions ~1 M. The neat samples were prepared from the freshly distilled liquids and placed in Wilmad PS-503 NMR tubes. The NV-14 spectrometer required an internal lock of ~10% by volume of benzene or Me_4Si. All NMR tubes were sealed under vacuum.

The optical measurements were obtained on a Cary 17 spectrometer at room temperature. The liquids were placed into shortened melting point capillaries by a syringe. These previously tared capillaries were weighed on a Cahn electrobalance. The capillaries were then broken in a volumetric flask and sufficiently diluted to give the appropriate concentrations of ~0.02 M. The solutions were then syringed into 0.5-cm cells and then sealed with silicone stopcock grease. The spectra were taken immediately with a 0.5-cm cell containing the solvent as a reference.

Magnetic susceptibility measurements were obtained with a PAR Model 155 vibrating sample magnetometer used with a homogeneous magnetic field produced by a Varian Associate 12-in. electromagnet capable of a maximum field strength of 12.5 kG. The magnetometer was calibrated with $HgCo(CNS)_4$.[11] A variable-temperature liquid-helium Dewar produced sample temperatures in the range 1.5–100 K which were measured by a calibrated GaAs diode placed approximately 0.5 in. above the sample. The liquids were placed in calibrated Kel-F screw top susceptibility capsules which were weighed on a Cahn electrobalance. The filled capsules were stored in Schlenk tubes under argon and were transferred to the susceptibility apparatus under flowing N_2. Samples of ~0.1 g were used.

Discussion

The reaction used for the syntheses of these new actinide amides is the same as employed previously for the large majority of transition metal amides[12]

$$MCl_4 + 4LiNR_2 \xrightarrow{Et_2O} M(NR_2)_4 + LiCl\downarrow$$

$$M = U, Th$$

$$R = -CH_2CH_2CH_3, -CH_2CH_2CH_2CH_3$$

Table I lists some of the physical properties of these actinide amides. Although the di-*n*-propyl and di-*n*-butyl actinide amides are the first reported actinide amides which are liquid at room temperature, this behavior is common in d-transition-metal amides.[1,12] The distillation temperatures of the corresponding thorium and uranium dialkylamides are quite similar.

The ^1H NMR spectra of the uranium and thorium amides in toluene-d_8 and THF-d_8 are given in Table II. The proton spectra of the thorium amides are almost identical with those of the free ligands as expected for a diamagnetic Th^{4+} ion. The ^1H NMR spectra of the uranium amides can be classified into two groups depending on the solvent used. The proton spectra of the uranium amides in toluene-d_8 have peaks asymmetrically placed about Me_4Si, and significantly shifted from the corresponding diamagnetic positions. As the distance of the proton from the U atom is increased, the magnitude of the shift decreases. Also, resolution of the spin–spin coupling occurs at the γ-carbon protons, suggesting that at this distance the effects of line width broadening due to the very fast electronic relaxation time of the paramagnetic U^{4+} ion are much diminished. If we assume that the U species in toluene solution is monomeric as found for the $U(NEt_2)_4$ compound,[8] then the most likely structure for the uranium *n*-alkylamides is tetrahedral. For this symmetry the pseudocontact term vanishes, and only the Fermi contact hyperfine interaction contributes to the paramagnetic shift.[13] This interaction would be of a similar magnitude for each of the uranium *n*-alkylamide compounds and would account for the similarily of the paramagnetic shifts in the series.

The same argument may be used for the ^1H NMR of the uranium *n*-alkylamides in ether solvents. Table II shows the great similarity of the shifts for the three compounds. It appears that the ether solvents complex the uranium amides and the solution structures are very similar. Therefore, the *g*-value anisotropy, the pseudocontact shifts, and the Fermi contact term are similar for each of the compounds, which results in similar ^1H NMR spectra for each of α, β, etc., protons in the alkyl chain for each compound.

The ^1H NMR spectra of the neat compounds are also given in Table II. These relative splittings and the resolution of the multiplets are the same as found in toluene solution but there is an absolute shift of 10–13 ppm upfield in the line positions due to the effects of the bulk susceptibility of the solution. These observations support our assumptions that the uranium *n*-alkylamides (and $U(NPh_2)_4$) do not coordinate with hydrocarbon solvents and that they are monomeric at room temperature in these solvents.

We have reported previously a possible monomer–dimer equilibrium for $U[NEt_2]_4$ in toluene-d_8 solution, which would change the symmetry about the U ion.[4] (The solid-state dimer has approximately C_{3v} symmetry about the U^{4+} ion.) Figure 1 shows the ^1H NMR spectra of $U[N(CH_2CH_2CH_3)_2]_4$ in toluene-d_8 at various temperatures. The monomeric species is clearly displayed at high temperatures but the changes in

Table II. Proton Magnetic Resonance Spectra of Some Uranium Amides[a] with Respect to Me_4Si (ppm)

Compd	Solvent	α	β	γ	δ	Temp, °C
$U(N(CH_2CH_3)_2)_4$[4]	Benzene-d_6	−13.0[b]	+5.4[c]			24
$U(N(CH_2CH_2CH_3)_2)_4$	Toluene-d_8	−8.4 s	+1.9 s	−0.4 t		25
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Toluene-d_8	−9.4 s	+3.1 s	−0.3 m	+0.5 t	19
$U(N(CH_2CH_3)_2)_4$[4]	THF-d_8	+18.2	+13.8			24
$U(N(CH_2CH_2CH_3)_2)_4$	THF-d_8	+19.8 s	+12.9 s	+8.04 t		26
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	THF-d_8	+17.9 s	+11.6 s	+6.5 s	+2.6 t	19
$U(N(CH_2CH_2CH_3)_2)_4$	Neat	+1.1 s	+11.4 s	+9.3 t		25
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Neat	+3.5 s	+16.5 s	+13.3 m	+14.1 t	25
$Th(N(CH_2CH_2CH_3)_2)_4$	Benzene-d_6	−2.7 t	−1.1 m	−0.5 m		25
$Th(N(CH_2CH_2CH_2CH_3)_2)_4$	Benzene-d_6	−2.95 t	−1.3 m	−1.0 m	−0.7 t	25

[a] Key: α = α-carbon proton, β = β-carbon proton, γ = γ-carbon proton, δ = δ-carbon proton, t = triplet, s = singlet, m = multiplet. [b] − = downfield relative to Me_4Si. [c] + = upfield relative to Me_4Si.

Table III. Peak Positions and Extinction Coefficients of $U(N(CH_2CH_2CH_3)_2)_4$ and $U(N(CH_2CH_2CH_2CH_3)_2)_4$ in Various Solvents

Compd	Solvent	Peak 1		2		3		4		5		6	
		λ, μm	ε	λ, μm	ε	λ, μm	ε	λ, μm	ε	λ, μm	ε	λ, μm	ε
$U(N(CH_2CH_3)_2)_4$[a]	Hexane	0.704	50	*b*		*c*		1.104	25	1.188	25	*c*	
$U(N(CH_2CH_2CH_3)_2)_4$	Pentane	0.705	39	*b*		*c*		1.105	24	1.180	24	*c*	
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Pentane	0.702	45	*b*		*c*		1.100	25	1.170	24	*c*	
$U(N(CH_2CH_3)_2)_4$[a]	Benzene	0.692	47	*b*		*c*		1.090	27	1.172	26	*c*	
$U(N(CH_2CH_2CH_3)_2)_4$	Benzene	0.705	44	*b*		*c*		1.105	32	1.180	30	*c*	
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Benzene	0.705	45	*b*		*c*		1.095	30	1.170	28	*c*	
$U(N(CH_2CH_3)_2)_4$[a]	Et_2O	0.638	28	0.660	24	0.718	15	0.990	20	1.070	32	1.302	19
$U(N(CH_2CH_2CH_3)_2)_4$	Et_2O	0.638	22	0.658	19	0.710	17	1.000	16	1.078	28	1.310	12
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Et_2O	0.640	24	0.665	19	0.710	17	1.005	17	1.070	30	1.305	18

[a] From ref 4. [b] Peaks were not split into two components. [c] Peaks masked by solvent bands.

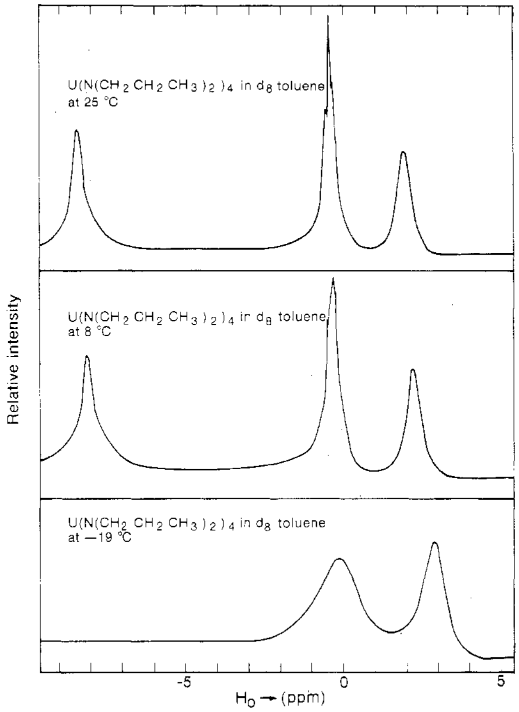

Figure 1. Proton magnetic resonance spectra of $U[N(CH_2CH_2CH_3)_2]_4$ in toluene-d_8 at various temperatures.

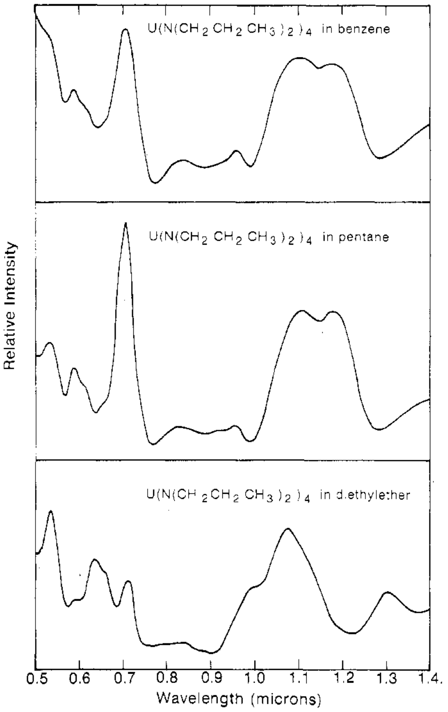

Figure 2. Optical spectra of $U[N(CH_2CH_2CH_3)_2]_4$ in various solvents at room temperature.

the spectra at low temperatures show definite signs of broadening and exchange. Unlike the $U(NEt_2)_4$ system where the dimer is observed clearly at ca. −43 °C, the uranium *n*-propylamide shows only broadening to ca. −60 °C at which point it freezes out of solution. The uranium *n*-butylamide exhibits similar behavior. These observations may be explained by a less favorable geometry due to greater steric hinderance for the formation of the dimeric species of the uranium *n*-propyl- and *n*-butylamides than for $U(NEt_2)_4$. Further work is underway on the temperature dependence of the ^1H NMR spectra.

The optical and near-IR spectra of the uranium *n*-propylamide in various solvents at room temperature are shown in Figure 2 and tabulated for both uranium amides in Table III. These spectra are almost identical with those of the previously published $U(NEt_2)_4$ and $U(NPh_2)_4$ in the same solvents.[4,6] As in the ^1H NMR spectra we suggest the spectra in the ether solvent are due to a U molecule associated with the complexing ether solvent molecules, whereas in hydrocarbon solvents the spectra are due to the uncomplexed tetrahedral U molecule. The almost identical spectrum for each of the uranium *n*-alkylamides in the same solvent shows that changing the alkyl chain has little effect on the f–f transitions. The major differences in the spectra come from changes in the first coordination sphere as shown by the effects of the ether solvent.

Table IV. Temperature-Dependent Susceptibility Values for Some Uranium Amides

Compd	C_M	μ_{eff}, μ_B	Θ, K	Temp, K
$U(N(CH_2CH_3)_2)_4$[4]	1.052	2.74	−4.8	20–100
$U(N(CH_2CH_2CH_3)_2)_4$	1.00	2.69	7.2	30–102
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	0.74	2.44	2.2	27–84
$U(N(C_6H_5)_2)_4$[6]	1.00	2.84	24.8	40–90

The inverse of the magnetic susceptibility of $U[N(CH_2CH_2CH_2CH_3)_2]_4$ in the temperature range 4.2–100 K is shown in Figure 3. A similar curve is found for $U[N(CH_2CH_2CH_3)_2]$. The data for the three *n*-alkylamides are collected in Table IV. In all cases there is Curie behavior down to ~30 K (20 K for $U(NEt_2)_4$) after which the inverse of the susceptibility tends to become less temperature dependent. The symmetry in the solid state of the two new uranium amides is unknown but the susceptibility data could be due to a ground-state singlet with a doublet state approximately ~35 cm^{-1} higher in energy. The effective moments of all the amides in the temperature range where they follow the Curie law are similar.

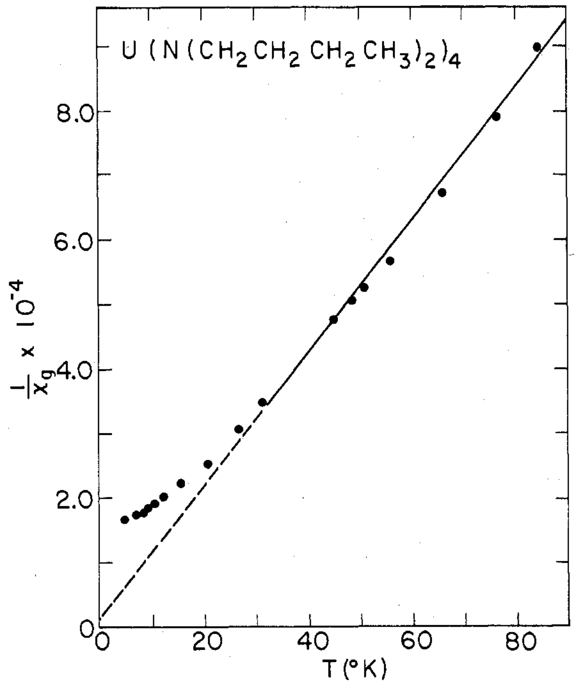

Figure 3. Inverse susceptibility of $U[N(CH_2CH_2CH_3)_2]_4$ vs. temperature. The straight line is the calculated inverse susceptibility in that temperature range with the parameters obtained from a least-squares fit as given in Table IV.

Conclusion

We have succeeded in the synthesis and characterization of some new uranium and thorium alkylamides, one of which was reported as being nondistillable in the original report of $U(NEt_2)_4$.[8] The uranium *n*-alkylamides and $U(NPh_2)_4$ have very similar spectral properties in various solvents. The ether solvents appear to complex each of the uranium *n*-alkylamides in the same fashion, while the hydrocarbon solvents do not appear to complex. The low-temperature magnetic susceptibilities in the solid state are similar. The analogous thorium *n*-alkylamides have been synthesized and appear to be light sensitive. These amides exhibit the expected diamagnetic behavior. Even though a number of new uranium and thorium amides have been synthesized and can be purified by distillation, there are d-transition-metal amides which sublime or distill for which the analogous actinide amides have not been isolated.[12,15] This may be because the uranium amides tend to oligomerize and/or be more thermally unstable than the corresponding d-transition-metal amides. Much work remains to be done on these interesting systems.

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Registry No. $U(N(CH_2CH_2CH_3)_2)_4$, 63833-51-2; $U(N(CH_2CH_2CH_2CH_3)_2)_4$, 63833-50-1; $Th(N(CH_2CH_2CH_3)_2)_4$, 63833-49-8; $Th(N(CH_2CH_2CH_2CH_3)_2)_4$, 63833-48-7; UCl_4, 10026-10-5; $LiN(CH_2CH_2CH_3)_2$, 4111-53-9; $ThCl_4$, 10026-08-1; $LiN(CH_2CH_2CH_2CH_3)_2$, 25440-26-0.

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A Nuclear Magnetic Resonance Study of Ligand Exchange on Dioxopentakis(trimethyl phosphate)uranium(VI) Ion and Its Triethyl Phosphate Analogue

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Ligand-exchange processes on $UO_2L_5^{2+}$ where L is either trimethyl phosphate (TMP) or triethyl phosphate (TEP) have been studied using ^1H and ^{31}P NMR techniques, respectively. In CD_2Cl_2 diluent the rate law for L exchange is rate = $5k_{ex}[UO_2I_5^{2+}]$, and the exchange mechanism is considered to be either D or I_d. Typical observed rate parameters are k_{ex}(260 K) = 95 ± 6 (32.2 ± 2.7) s^{-1}, $\Delta H^* = 6.0 \pm 0.3$ (10.4 ± 0.4) kcal mol^{-1}, $\Delta S^* = -26.1 \pm 2.3$ (−11.3 ± 1.4) cal deg^{-1} mol^{-1} for solutions in which $[UO_2L_5^{2+}]$ = 0.039 (0.139) M, [L] = 0.198 (0.745) M, and $[CD_2Cl_2]$ = 12.18 (11.21) M where in each case the first magnitude refers to the TMP system and that in parentheses refers to the TEP system. From a comparison of $\Delta H^*/\Delta S^*$ linear free energy relationships it is concluded that the surface charge density at the uranium center seen by the equatorial ligands in $UO_2L_5^{2+}$ lies between that on the tervalent aluminum and the divalent first-row transition-metal centers in AlL_6^{3+} and ML_6^{2+}, respectively.

Introduction

The dioxouranium(VI) ion presents the unusual opportunity to study substitution processes in which transition state flexibility is likely to be restricted to the equatorial plane as a consequence of the relatively rigid dioxouranium(VI) axis.[1–6] Of considerable interest is the extent to which the two inert oxo ligands[7,8] modify the reactivity of the formally sexavalent uranium center toward ligand substitution in the equatorial plane. Ligand-substitution studies[9–11] in aqueous solution (and theoretical treatments[12]) indicate that the effective charge on the uranium center is considerably less than six, but the absence of a detailed mechanistic characterization of water exchange on $UO_2(H_2O)_4^{2+}$ [13] necessarily injects some uncertainty into the detailed interpretation of these studies. Such difficulties are much reduced in studies of exchange of a ligand L on $UO_2L_5^{2+}$ species[14–16] as typified by the systems in which